



Letter to the Editor

Reply to the Letter to the Editor concerning the comments of M.A. Banares and M.O. Guerrero-Pérez to the article “Glycerol conversion to acrylonitrile by consecutive dehydration over WO_3/TiO_2 and ammoxidation over $\text{Sb}-(\text{Fe,V})-\text{O}”$ [1].



Keywords:

Glycerol
Ammoxidation
Direct reaction

Dear Editor,

This is with a great interest that we have read the letter of Prof. Miguel A. Banares and Dr. Olga Guerrero-Perez commenting our article “Glycerol conversion to acrylonitrile by consecutive dehydration over WO_3/TiO_2 and ammoxidation over $\text{Sb}-(\text{Fe,V})-\text{O}”$ [1].

In the aforementioned work, reporting an indirect pathway of acrylonitrile synthesis from glycerol *via* acrolein as an intermediate, we have also studied in a previous step the direct ammoxidation of glycerol to acrolein. This latter would provide some evident advantages over the indirect process since it would require only one reactor. Thus, in the beginning of our work we tried to reproduce the results of Prof. Banares and Dr. Guerrero-Perez who reported the direct ammoxidation of glycerol in 2008 [2]. As mentioned in our manuscript, we did not succeed.

Against the assumption of Prof. Banares and Dr. Guerrero-Perez expressed in their letter, we did try to reproduce the synthesis of the catalyst supported on alumina that they employed according to the procedure described in their article. Please, refer to the electronic Supplementary information of our article, where it is clearly stated that the VSbO_4 catalyst used for the direct ammoxidation test was prepared as described by Banares et al. [3]. It seems that there is here a confusion with the catalyst that we used for the ammoxidation of acrolein, which has been prepared following Nilsson's procedure [4].

The detailed synthesis of the catalyst we used for the direct ammoxidation is as follows: 0.9 g of ammonium metavanadate (Aldrich) was dissolved under stirring in 100 mL of hot water (80 °C). After complete dissolution, 1.1 g of antimony oxide (Aldrich) were added. The solution was left another 80 min at 80 °C before 3 g of γ -alumina (PURALOX®, SASOL) were added. The solvent was evaporated at 80 °C under reduced pressure of 0.3 bar. The resulting solid was dried at 115 °C before it was calcined in static air at 400 °C for 4 h (heating ramp 10 °C/min).

The resulting theoretical Sb/V ratio is 0.98, which is quite close to 1, the ratio necessary to achieve high yields according to Prof. Banares and Dr. Guerrero-Perez. The specific surface of the as-prepared catalyst was 94 m²/g with a pore volume of 0.23 cm³/g and an average pore diameter of 7 nm. Hence, the specific surface area is close to the one reported by Banares et al. [3] even though the comparison is not straightforward since the

type of γ -alumina employed during Banares et al.'s work was not given.

Hence, we again explicitly state that the catalyst employed for the direct ammoxidation was prepared according to the method described by Banares et al. [3]. This catalyst is not identical to the Sb-V catalyst employed for the ammoxidation of acrolein to acrylonitrile, which was prepared according to the method of Nilsson et al. [4]. We thus assume that we do have reproduced at our best the catalyst synthesis as well as the reaction conditions employed by Banares et al. [2] considering all the data available. Nevertheless, the synthesis of catalysts and reproduction of catalytic tests based on bare literature data are never easy, whereby we would appreciate to receive the original sample of Prof. Banares. Alternatively, we kindly accept the invitation of Prof. Banares to host a member of our group and thank him for this proposal. We would like to underline here the fact that our aim was absolutely not to discredit the work of Prof. Banares' estimated group and that we will be very glad to collaborate with this group on this challenging topic.

Concerning the remarks about the catalytic performances observed in our test, we first of all want to apologize for our error when claiming that the observed full conversion in our case was in agreement with Prof. Banares and Dr. Guerrero-Perez's work. As they correctly mention, the conversion observed in their tests never reached 100%. We also agree with that the sum of selectivity in our case was 69% (*cf.* electronic Supplementary information of Ref. [1]), meaning that nearly one third of the products were not identified. Hereby, several hypotheses arise, such as the formation of carbonaceous species or unknown compounds, which were not identified by the employed chromatographic methods. At this date, we cannot answer the question about the remaining 31% products. Nevertheless, we clearly observed that we never obtained more than 2% acrylonitrile.

Finally, Prof. Banares and Dr. Guerrero-Perez correctly mentioned that in an initial work of J-L. Dubois, the ammoxidation of glycerol was described, whereby also the possibility of a one-step process was evoked [5]. This patent has been filed (Feb 16 2007 for French priority) prior to the submission of the publication from Prof. Banares, and *per se* cannot be considered as a duplication of his work but rather as prior art. Although direct conversion of glycerol to acrylonitrile is included in the first claim, the claim 3 indicates that the reaction can be performed after an initial dehydration step. A possible explanation for the discrepancy in the results might be due to the fact that it seems that Prof. Banares and his team have chosen to work within the explosion range of the reaction mixture. This point should be carefully checked and possible gas phase reactions would explain the difficulties to duplicate the results. Literature provides flammability diagrams for propylene–NH₃–air mixtures, and acrolein–O₂–N₂ mixtures, which suggest a possible risk if glycerol behaves as propylene.

In addition, the reaction done in Prof. Banares' publication seems to have been carried out in absence of water (pure glycerine) while experiments done in this work have been carried out in presence

of aqueous glycerine. The absence of water in the reaction stream should have a very strong impact on the results.

In fact, when assuming that the direct pathway also involves the formation of acrolein as an intermediate (which most probably remains adsorbed on the surface of the catalyst), the direct ammoxidation will require a bi-functional catalyst exhibiting acid and redox properties for the dehydration of glycerol to acrolein and the successive ammoxidation of acrolein to acrylonitrile, respectively. Hereby, one of the main problems lies in the co-feeding of ammonia for the ammoxidation reaction, which inevitably blocks the acid sites. Thus, increased reaction temperature will be required which promotes the thermal deactivation of glycerol. For these thermodynamical reasons, the direct pathway remains a challenge. Hence, at the current state the article of Banares et al. [2] is the only report on the direct ammoxidation of glycerol in gas-phase. As a matter of fact, most of the works on the subject rather focus on the development of the indirect process, even though these will inevitably require more than one reactor.

To conclude, as mentioned above, we are open for collaborating in the near future with Prof. Miguel A. Banares and Dr. Olga Guerrero-Perez on this very interesting but still challenging reaction.

Sincerely,

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References

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10 November 2013

13 November 2013

Available online 21 November 2013